CRYSTAL FIELD SPECTRA OF $3d^n$ IMPURITIES IN II-VI AND III-V COMPOUND SEMICONDUCTORS[†]

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ABSTRACT

The spectra of $Fe(d^6)$ in ZnSe, ZnTe, CdS, CdTe, GaP and GaAs, and of $Co(d^7)$ in ZnSe, ZnTe, GaP and GaAs, are presented. It is found that a crystal field description is useful even in such covalent materials. The crystal field splitting, Δ, depends on the impurity but, for a given impurity, Δ varies by less than 25% through the II-VI series. The Racah parameter B is strongly dependent on the host crystal and can decrease to less than a third of the free-ion value. From plots of the variation of B and Δ with properties of the impurity or host crystal, the spectra of hitherto unexplored systems may be predicted.

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INTRODUCTION

In recent years a number of studies have been made of the optical absorption spectra of $3d^n$ transition metal impurities in II-VI semiconductors. Examples are the work of Pappalardo and Dietz[1] with CdS, and of Weakliem[2] with ZnO, ZnS and CdS. Loescher et. al.[3] extended the area to the III-V semiconductors by investigating $Co(d^7)$ in GaP. It is found that the spectra are well described by crystal field theory as long as the Racah parameters B and C and the crystal field splitting Δ are taken as quantities to be determined by experiment. There is as yet no theoretical justification for this fact.[4] A point charge model for the lattice is clearly inapplicable, and molecular-orbital calculations have not yet reached the stage at which they can do more than qualitatively reproduce some experimental observations, when the host lattice is as strongly covalent as the ones under consideration.

To elucidate some of the operative mechanisms, we have investigated the way in which the parameters B and Δ vary with impurity and with host lattice. Iron (d^6) and cobalt (d^7) were chosen for particular attention. They are easily introduced into the appropriate lattices. Iron (d^6) in tetrahedral coordination has a first excited level whose position is independent of B, so information on the variation of Δ is simply obtained. Cobalt (d^7) has a distinctive spectrum in a convenient spectral range, from which both Δ and B may be obtained.

EXPERIMENTAL

The II-VI and III-V semiconductors were in the form of solid ingots which were either single crystal or coarsely polycrystalline. Iron or cobalt were normally introduced by evaporating a layer of metal onto a slice of semiconductor and then diffusing at high temperature. The ZnSe: Co samples were grown by Dr. S. J. Bass of SERL by melting ZnSe in a closed ampoule in the presence of cobalt oxide. The ZnSe: Fe samples were also grown by Dr. Bass, using vapor transport in a closed tube with a trace of halide as transporting agent. (Without the halide the ZnSe transports but not the iron.) After polishing, the samples were mounted on the cold-finger of a Dewar which had sapphire windows. A carbon resistance thermometer was used to monitor the sample temperature. Because of the low thermal conductivity of materials containing $Fe(d^6)$, discovered by Slack[5], it was found that samples nominally at liquid helium temperatures were in fact at temperatures ranging up to 8^oK. Spectra were measured on a Cary 14 IR spectrophotometer out to 2.5μ (4000 cm^{-1}) and on a Perkin-Elmer 621 spectrophotometer for longer wavelengths.

From arguments similar to those used by Loescher et. al.[3] for GaP: Co, it appears that the spectra are due to iron or cobalt on substitutional cation sites.

EXPERIMENTAL RESULTS

(a) Iron(d^6)

The spectra of Fe(d^6) in the zinc-blende crystals ZnSe, ZnTe, CdTe, GaP and GaAs, and in the wurtzite crystal CdS, are shown in Fig. 1. There are a few closely-spaced zero-phonon lines at low energies with widths less than the resolution used, namely 6 cm^{-1}. At higher energies there is a broader, more complex structure. Slack et. al.[6] have found similar spectra for iron in cubic ZnS and CdTe.

Low and Weger[7] have given expressions for the crystal field levels of a d^6 configuration in a cubic field, with spin-orbit interactions included. In a tetrahedral field the ^5D term is split into the levels shown in Table I, in which the energies are given to second order. We interpret the sharp lines as being transitions from the ^5E levels to the lowest level of $^5T_2$, the decrease of intensity with decrease in energy reflecting the Boltzmann distribution over the levels. Table II gives the position of the strongest sharp line, the separation of the lower energy lines from it, and a calculated set of separations taking as representative values $\Delta = 2700$ cm^{-1} and $\lambda = -80$ cm^{-1}. (The free ion value is -103 cm^{-1}.) There appears to be no static Jahn-Teller effect, for otherwise we should have a different line pattern, as may be seen from the calculations of Low and Weger. Goodenough[8] has given arguments to show that static Jahn-Teller distortions of tetrahedral Fe(d^6) in moderately covalent hosts should be small, in agreement with our observations.

The structure at higher energies is harder to interpret, partly because it is difficult to distinguish between vibronic and electronic transitions. From Table I it is seen that there should be two lines at $2|\lambda|$ and $5|\lambda|$ beyond the sharp lines, each split by second order interactions. If the two broad structured bands in the spectra are attributed to these transitions, then the value of λ varies strongly from host to host, ranging down to half the free ion value. This is in contradiction to the observed splitting of the ground state. A possible explanation lies in the Ham effect[9], in which dynamical Jahn-Teller distortions reduce the apparent value of some first-order splittings, but may not effect second-order interactions. Unfortunately, we have no way of estimating the magnitude of the effect. Indeed the apparent reduction of λ may be so great that the transitions to the $^5T_2$ levels are all contained in the structure close to the main sharp line[6]. Since the fine structure is not the primary concern of this paper, we simply note that the main sharp line will have an energy

$$E = \Delta + 3\gamma\lambda + \frac{138}{5} \frac{\lambda^2}{\Delta} \tag{1}$$

where γ is a reduction factor lying between 0 and 1.

In the wurtzite structure, the cation site has approximate tetrahedral symmetry, together with a small axial component. Correspondingly, the spectrum of CdS: Fe is similar to that of the zinc-blende materials but shows small additional splitting. Four lines are resolved, and from these we deduce $\Delta = 2800$ cm^{-1}, $\lambda = -95$ cm^{-1}, and the trigonal axial field component, b, is $+70$ cm^{-1}.

(b) Cobalt(d^7)

Pappalardo and Dietz[1] have discussed in detail the fitting of the spectrum of CdS: Co to a crystal field level scheme, and Weaklien[2] has done the same for ZnO: Co, ZnS: Co and CdS: Co. We find similar spectra for Co(d^7) in ZnSe, ZnTe and CdTe, as shown in Fig. 2. Just beyond the visible region there is a strong peak due to the $^4A_2(F)$ - $^4T_1(P)$ transition, showing structure caused by spin-orbit splitting and mixing with nearby doublets. Further into the infra-red there is another absorption due to the $^4A_2(F)$ - $^4T_1(F)$ transition, and near 3500 cm^{-1} is the very weak absorption due the symmetry forbidden $^4A_2(F)$ - $^4T_2(F)$ transition. Table III gives the values of B and Δ as deduced from the spectra.

Loescher et. al.[3] measured the spectrum of GaP: Co at liquid nitrogen temperature and deduced values for B and Δ. At helium temperatures, the spectrum, Fig. 2(d), is better resolved. It is not possible to fit the absorption peaks exactly with crystal-field expressions, but the values B = 290 cm^{-1}, Δ = 5400 cm^{-1}, give a fit to within 200 cm^{-1}. In GaAs: Co the breakdown of the crystal field approach has gone further. The distinctive $^4T_1(P)$ absorption is clearly visible in Fig. 2(e), even though it is close to the main absorption edge of GaAs. Three other bands are seen. Without additional experiments it is not possible to identify them, since $^4T_1(F)$ will be interacting with nearby doublets. No set of values of B, Δ, and λ fit the spectrum exactly, but it appears that Δ is about the same as for GaP: Co, while B must be less than a quarter of the free-ion value.

DISCUSSION

It may be seen from Eq. 1 that for $Fe(d^6)$, the value

of Δ is close to the energy of the main sharp line. Figure 3 shows

the main line energy in II-VI compounds as a function of atomic spacing

in the host lattice. The variation in energy is not great, but there

is a definite trend for Δ to decrease as the crystal spacing increases

and the crystal becomes more covalently bonded. In gallium phosphide,

iron with a d^6 configuration has accepted an electron and is negatively

charged with respect to the gallium atom that it replaces. The value

of Δ for GaP: Fe is 15% greater than it would be for a II-VI compound

with the same lattice constant, while for GaAs: Fe the corresponding

figure is 8%.

Inspection of Table III shows that, for $Co(d^7)$ in the

II-VI series, the variation of Δ is again rather small. Any

systematic variation is largely masked by uncertainties in the para-

meter values, but again Δ tends to decrease as the crystal becomes

more covalent. Cobalt(d^7) in GaP is negatively charged and the value

of Δ is again increased over that expected for a corresponding

II-VI compound, this time by about 50%.

Since Δ is roughly constant for a given $3d^n$ impurity

in the II-VI series, it is meaningful to ask how Δ varies with

impurity, irrespective of the host crystal. Before doing so, we

have to consider one complication. When comparing electronic transi-

tion energies, one should use the barycentres of the absorption

bands[11], not the zero-phonon line positions. In the semiconductors

discussed in this paper, the distinction is unimportant except for

manganese (d^5) and iron (d^6). The values of Δ for Fe(d^6) used

here are therefore greater by about 200 cm^{-1} than those used above.

Figure 4 shows Δ for divalent transition metal impurities in II-VI

compounds. The data were in part culled from the literature, while

other points came from the present work and from the unpublished

absorption spectra measured by one of us (JWA) for Ti(d^2), V(d^3) ,Cr(d^4)

and Ni(d^8) in ZnSe. Because of special difficulties of interpretation,

the values for Mn(d^5) are open to question. It can be seen that the

data exhibit a definite pattern, with Δ being greatest near filled

or half-filled shells. We have no explanation for this. Slack[5]

has observed a superficially similar behavior of the covalent radii

of the divalent atoms, but the maxima and minima in the radii occur

at one atomic number greater than the corresponding feature in Δ.

Weakliem[2] has pointed out a correlation between the

Racah parameter B and the anion polarizability for Co(d^7) in

various compounds. Our results enable this to be extended to much

lower values of B. Because we are also interested in III-V compounds,

it is more convenient to use the electronic dielectric constant (i.e.,

n^2, the square of the infra-red refraction index), as being more accessi-

ble than the anion polarizability. Figure 5 shows the relation between

n^{-2} and β, where β is the ratio of the value of B in the crystal

to that in the free ion. A simple correlation exists. It is interest-

ing to note that the point for GaP is not far from the line for the

II-VI compounds. The correlation is intelligible if the reduction

of B is due to screening of d-orbital electrostatic interactions

by the bonding electrons. If, as a consequence of the screening, the

d-orbitals were expanded over many lattice sites (an extreme case not
realized in practice, of course), then they would feel the full di-
electric screening and β would be equal to n^{-2}. If the screening
were small, then the d-orbitals would behave much as if they were in
a free ion, and β would become unity. In accordance with this idea,
at large n the line of Fig. 5 approaches the line $\beta = n^{-2}$, and at
small n it approaches the line $\beta = 1$.

The value of β for $Ni(d^8)$ behaves similarly. There
is as yet insufficient evidence to discuss the variation of β in
other configurations.

CONCLUSIONS

It is clear from the discussion that there are two
quite separate effects on d-orbital energies when a $3d^n$ impurity is
placed substitutionally in II-VI or III-V semiconductors. The first
is a reduction of the electrostatic interactions , and the second is a
splitting of the d-levels by the tetrahedral environment. It is also
clear that the reduction of B is at least as important as the
splitting, Δ, in governing transition energies. Any theory which
attempts to explain the magnitude of Δ but which ignores, or fails
to explain, the magnitude of β must be of very limited validity for
the materials discussed here. Experimentally, the value of β is
found to be strongly dependent on the host crystal, while Δ is
mainly a function of the impurity itself. There is no direct corre-
lation between the two, although broadly speaking both β and Δ
decrease as the crystal becomes more covalent.

It may well be that the use of a crystal field description will turn out to be an equivalent representation of the real, complicated situation, in the same sense that the use of operator equivalents can simplify a more complicated problem.[4] Many of the effects of covalency are then taken into account by using empirical values of B and Δ. The calculation of ground-state energies of impurities relative to the conduction or valence band of the host crystal[12] was carried through in this spirit. The importance of the reduction of the electrostatic parameters is apparent when this calculation is performed for ZnS and for GaAs. Energy level differences of the order of leV arise from differences of B, whereas differences of Δ only contribute of the order of 0.leV. Our results suggest that other calculations, such as those of Powell et. al.[13] on the higher order splitting of $^6A_1$ in Mn(d^5), might give closer agreement with experiment for covalently bonded materials if, instead of taking B as constant and Δ as variable, one took Δ as constant and B as variable.

Finally, two practical points emerge. Firstly, a crystal field description in which the parameters are empirical is useful even for materials as covalent as GaP or CdTe although it is beginning to break down for GaAs. Secondly, the values of the parameters can often be estimated by means of the correlations given here, a result which is of considerable use in interpreting spectra.

ACKNOWLEDGMENTS

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TABLE I   Energy levels to second order of d^6 in a tetrahedral field.

Δ = crystal field splitting, λ = spin-orbit coupling parameter.

$$
^5T_2 \quad
\begin{aligned}
&\Delta - 2\lambda + 24\ \lambda^2/\Delta \\
&\Delta - 2\lambda + 12\ \lambda^2/\Delta \\
&\Delta - 2\lambda + \frac{12}{5}\ \lambda^2/\Delta \\[1em]
&\Delta + \lambda + 12\ \lambda^2/\Delta \\
&\Delta + \lambda + 6\ \lambda^2/\Delta \\[1em]
&\Delta + 3\lambda + \frac{18}{5}\ \lambda^2/\Delta
\end{aligned}
$$

$$
^5E \quad
\begin{aligned}
&0 \\
&- 6\ \lambda^2/\Delta \\
&- 12\ \lambda^2/\Delta \\
&- 18\ \lambda^2/\Delta \\
&- 24\ \lambda^2/\Delta
\end{aligned}
$$

TABLE II   Position of the main sharp line in $Fe(d^6)$ absorption spectra at liquid helium temperatures, and energy separation of lower-energy lines from the main line. Calculated values for Δ = 2700, λ = -80. All energies in cm^{-1}.

	ZnS[6]	ZnSe	ZnTe	CdTe	GaP	GaAs	Calc.
Main line	2947	2738	2486	2282	3344	3002	
Separation 1	0	0	0	0	0	0	0
2	15	17	15	17	13	14	14
3	26	28			24		28
4	46	43			39		43

TABLE III   Crystal field parameters for $Co(d^7)$ in zinc-blende and wurtzite semiconductors

Host	B	Δ	Ref.
ZnO	775 cm^{-1}	3900 cm^{-1}	2
"	700	3900	10
ZnS	610	3550	2
ZnSe	570	3800	
ZnTe	460	3450	
CdS	610	3300	2
"	664	3160	1
CdTe	485	3150	
GaP	290	5400	3

Fig. 1(a) - (f)   Spectra of $Fe(d^6)$ at liquid helium temperature in tetrahedrally-coordinated semiconducting compounds.

Fig. 2(a) - (e)   Spectra of $Co(d^7)$ in tetrahedrally-coordinated semi-conductors.

        Fig.2(a)   - liquid nitrogen
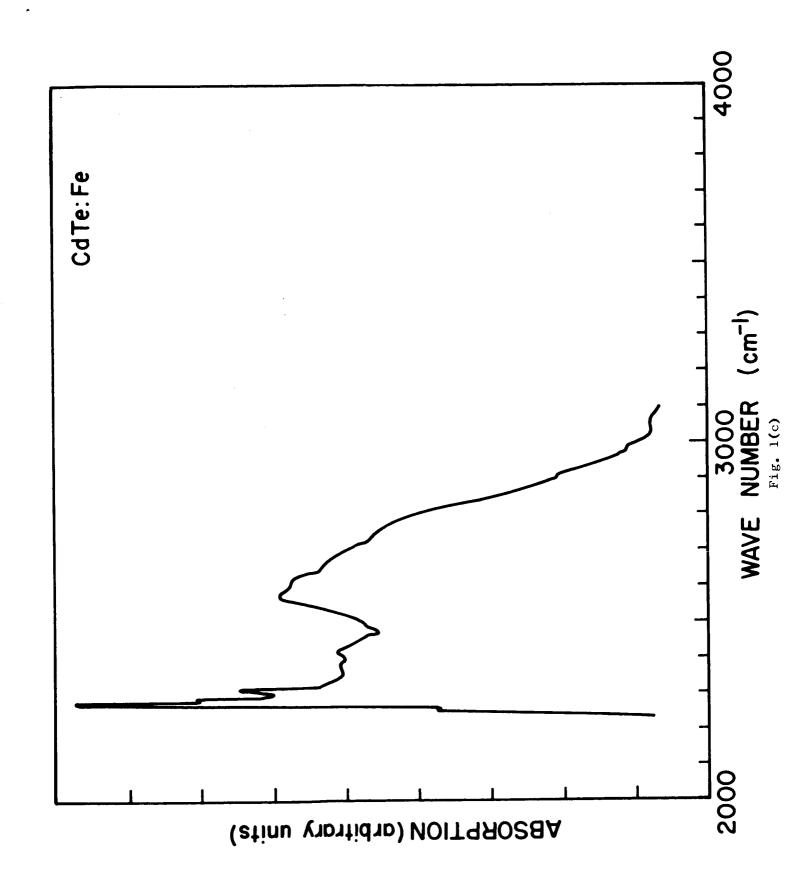
        Fig.2(b) - (e) - liquid helium

Fig. 3   Variation of the position of the strongest sharp line in the spectrum of $Fe(d^6)$ with atom spacing of the host crystal.

Fig. 4   Variation of the crystal field splitting Δ through the first transition series for impurities in II-VI semiconductors.
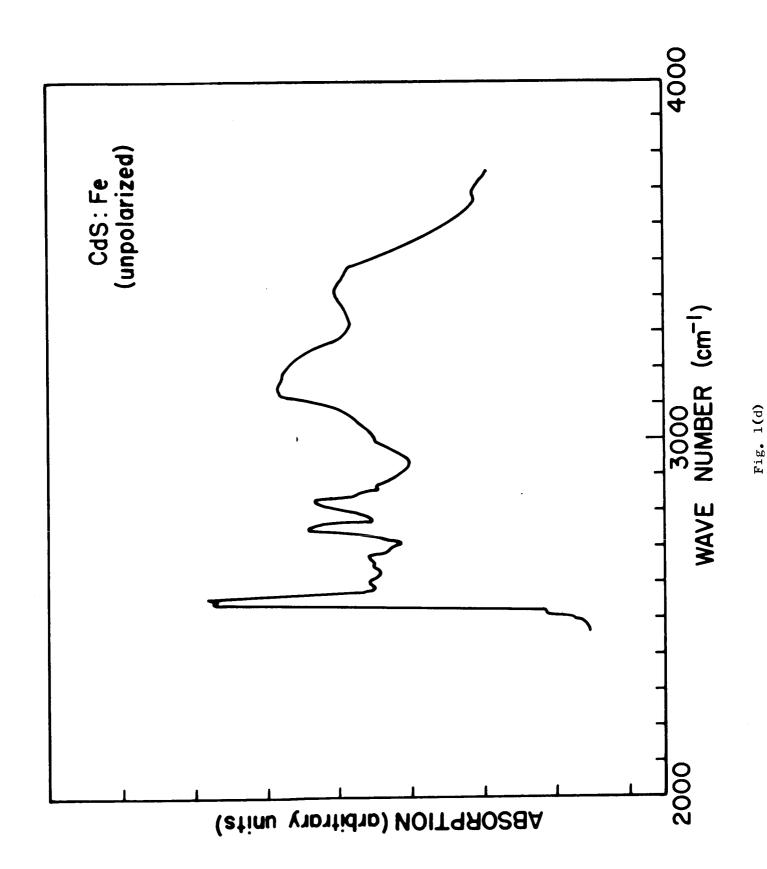
        Key   ⊙ ZnO   ∇ ZnTe

                   ⊡ ZnS   ✕ CdS

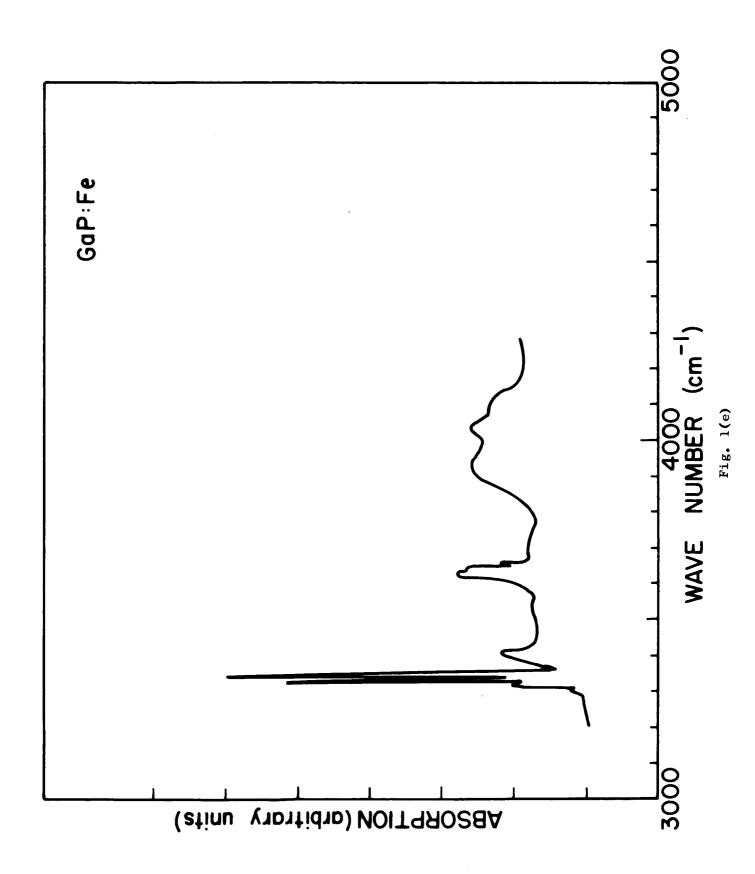   △ ZnSe   + CdTe

Fig. 5   Variation of the Racah parameter reduction factor β with n^{-2}, where n is the infra-red refractive index, for $Co(d^7)$.
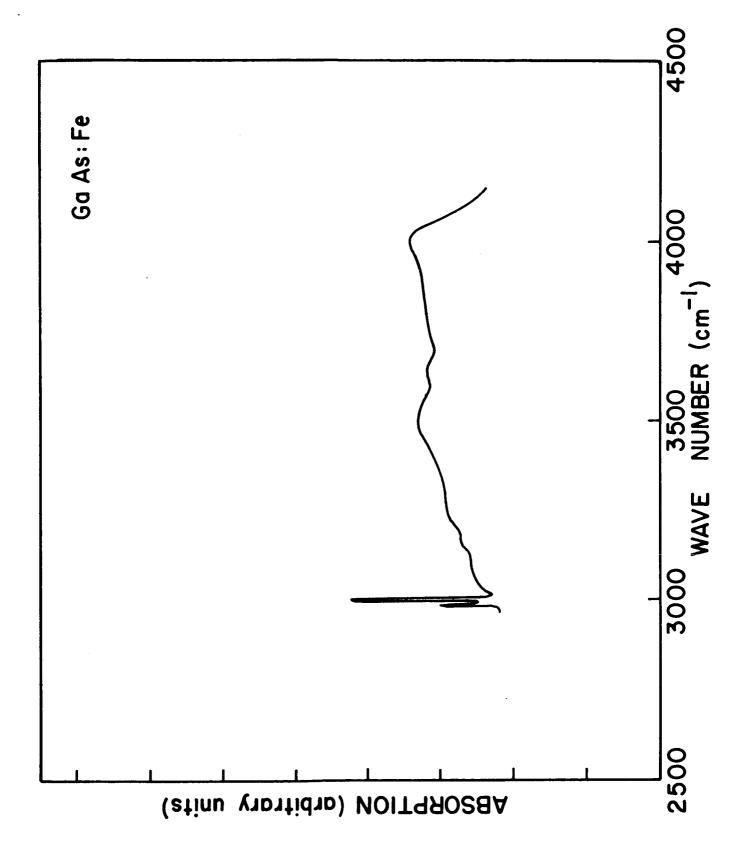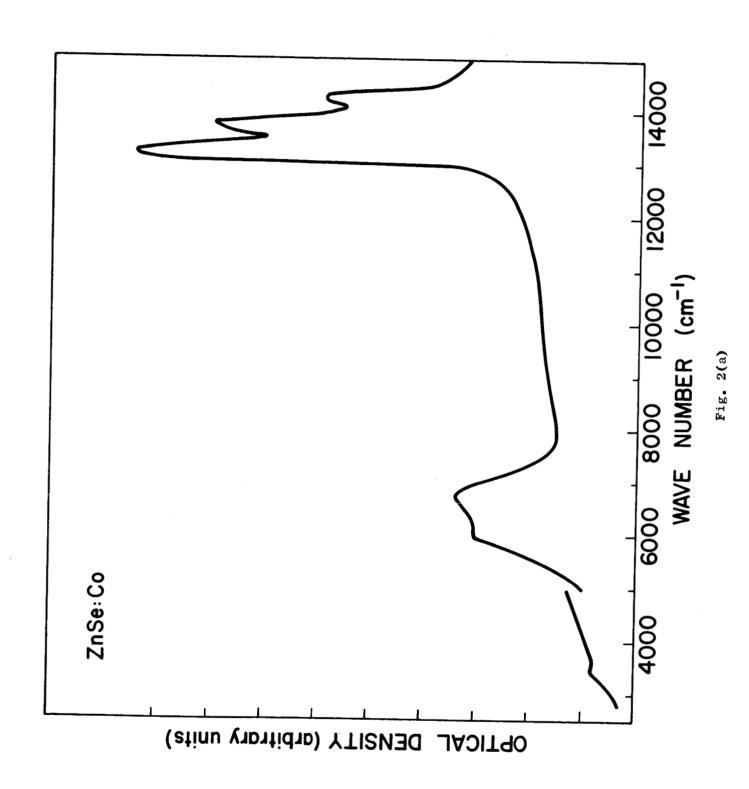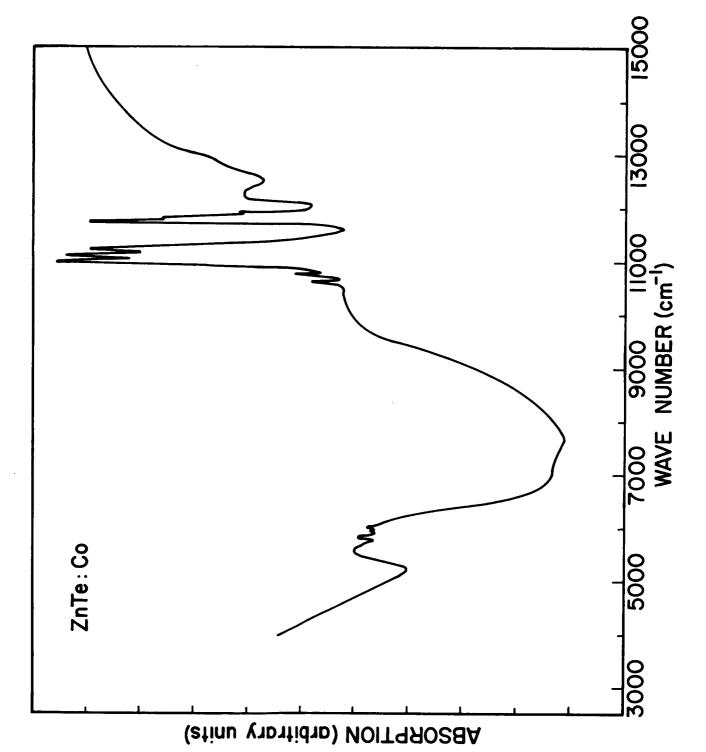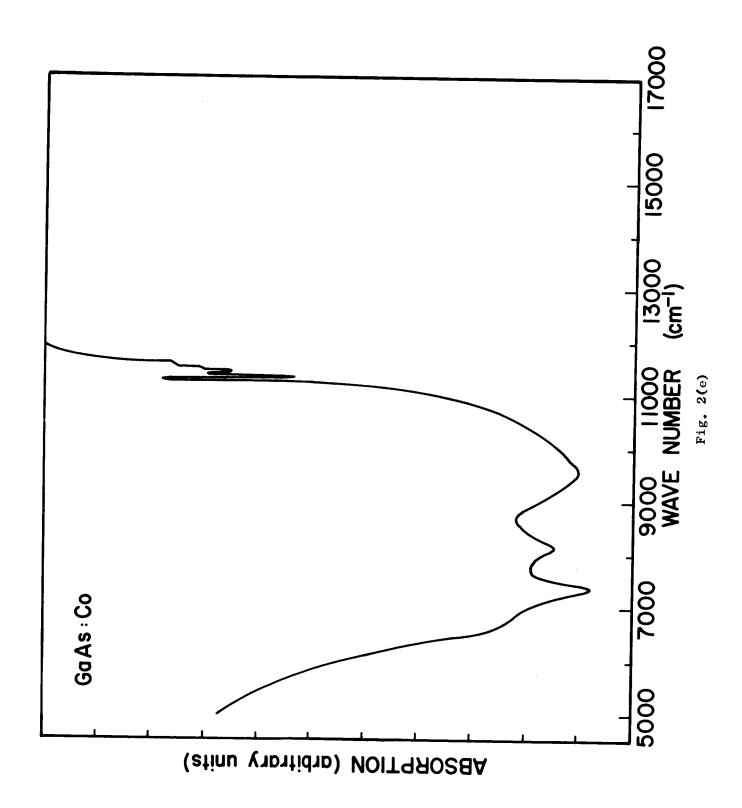
ZnSe:Fe

ABSORPTION (arbitrary units)

WAVE NUMBER (cm⁻¹)

Fig. 1(a)

ZnTe:Fe

ABSORPTION (arbitrary units)

WAVE NUMBER (cm^{-1})

2000   3000   4000

Fig. 1(b)

CdTe:Fe

ABSORPTION (arbitrary units)

WAVE NUMBER (cm⁻¹)

Fig. 1(c)

CdS: Fe
(unpolarized)

ABSORPTION (arbitrary units)

WAVE NUMBER (cm^{-1})

2000   3000   4000

Fig. 1(d)

GaP:Fe

ABSORPTION (arbitrary units)

WAVE NUMBER (cm^{-1})

Fig. 1(e)

Ga As: Fe

ABSORPTION (arbitrary units)

WAVE NUMBER (cm^{-1})

Fig. 1(f)

ZnSe:Co

OPTICAL DENSITY (arbitrary units)

WAVE NUMBER (cm^{-1})

4000 6000 8000 10000 12000 14000

Fig. 2(a)

ZnTe:Co

ABSORPTION (arbitrary units)

WAVE NUMBER (cm⁻¹)

Fig. 2(b)

CdTe:Co

ABSORPTION (arbitrary units)

WAVE NUMBER (cm^{-1})

Fig. 2(c)

GaP : Co

ABSORPTION (arbitrary units)

WAVE NUMBER (cm⁻¹)

Fig. 2(d)

Fig. 2(e)

Fig. 3

Fig. 4

Fig. 5